COATINGS. ENAMELS

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EFFECT OF ALKALI METAL OXIDES ON THE PROPERTIES OF TITANIUM CONTAINING GLASS ENAMELS

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The effect of the ratio of three alkali oxides on the physical and chemical properties of titanium-containing enamels has been investigated and their optimal concentrations have been determined. Acid resistant enamel for steel utensils has been developed.

Titanium-containing glass enamels have an important place in the enameling industry and are widely used for enameling steel utensil and sanitary ware. The quality requirements for enameled utensils are becoming increasingly more stringent with respect to both the eutectic properties and corrosion resistance. Specifically, the requirements for the migration of harmful components from coatings into food solutions are becoming more and more stringent. The problem of increasing the chemical resistance of white utensil enamels is becoming more complicated because of the limited choice of the initial components for synthesizing glass frit.

The objective of our investigations is to increase the chemical resistance of titanium enamels by introducing small quantities of lithium oxides and optimizing the ratio of the alkali oxides in them. Lithium oxide is known to increase the acid-resistance of glass substantially, and it is present in virtually all enamels used for chemical apparatus [1]. In this connection, the properties of glasses with different ratios of the alkali oxides (Na_2O, K_2O, Li_2O) and constant content of all other components (SiO_2, B_2O_3, TiO_2, Al_2O_3, MgO, P_2O_5, F) were studied (the B_2O_3 content was 10%).[2] The total content of the alkali oxides in the glasses studied was 16%. The Li_2O content was varied in the range 0 – 6%, Na_2O in the range 6 – 16%, and K_2O in the range 0 – 8% (Fig. 1).

The present work is a continuation of the investigations of titanium-containing alkali glasses for white glass-enamel coatings [2, 3].

Chemically pure reagents and OVS-015 quartz sand from the Novoselkovskoe deposit were used to synthesize the experimental glasses. The glasses were made in porcelain crucibles in an electric furnace with Silit heaters at temperature 1350°C with 30 min soaking.

The glasses were completely made under the chosen conditions and were of good quality. Opalescence was observed in glasses containing 6% Li_2O cast in the form of a small cake.

For the titanium-containing glasses synthesized, where the ratio of the alkali metal oxides was varied, the CLTE, the softening onset temperature, the flowability, the acid-resis-

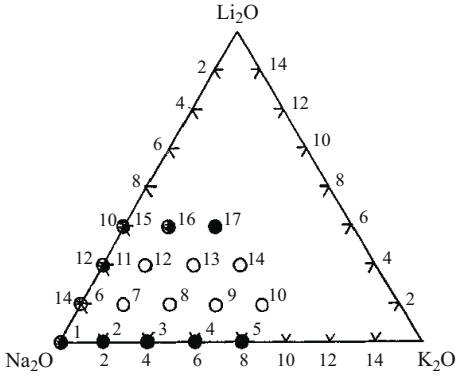

Fig. 1. Region of chemical compositions of the experimental glasses in the system $R_2O – R_2O_3 – RO – SiO_2 – TiO_2 – P_2O_5 – F$ and the crystalline phases formed during heat treatment (the content of all other components is constant): ○) anatase; ●) rutile; ∗) quartz modification.

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[2] Here and below — the molar content.

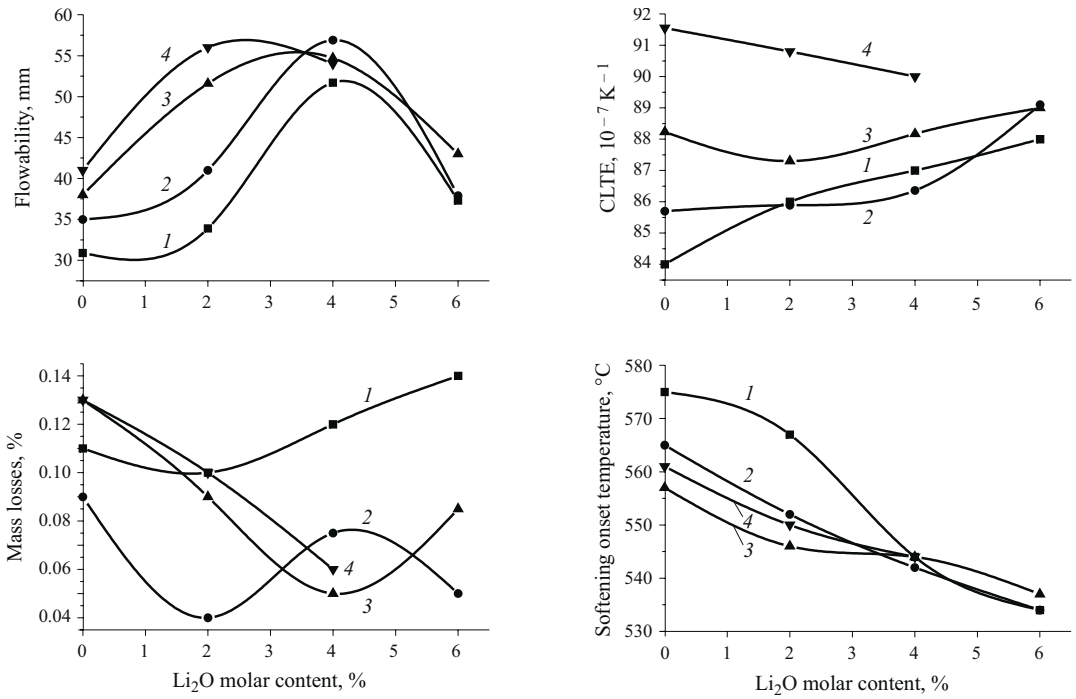

Fig. 2. Effect of alkali metal oxide on the flowability at 850°C, chemical resistance in 4% acetic acid, CLTE, and softening onset temperature of the experimental glasses: *1*, *2*, *3*, and *4*) K_2O molar content 0, 2, 4, and 6%, respectively.

tance, the capability of forming a coating, and the whiteness of the coating were determined. The results of the investigations are presented in Table 1 and in Fig. 2. The investigations showed that substituting potassium oxide for sodium oxide in lithium-free glass or 2 – 4% Li_2O glass increases the flowability and the CLTE and decreases the softening onset temperature. The chemical stability of the glasses remains essentially unchanged. For 4 and 6% Li_2O, substituting K_2O for Na_2O within the experimental limits has virtually no effect on the properties of the glasses. Introducing small amounts (2%) of Li_2O instead of Na_2O has the greatest effect on the flowability, the CLTE, the softening onset temperature, and the chemical resistance of the glasses. As the Li_2O content is increased further, the properties of the glasses change more slowly. When Li_2O is introduced, the flowability of the glasses increases substantially at first, but it decreases sharply to 43.0 – 37.3 mm for 6% Li_2O because the samples crystallize. It should also be noted that the resistance of the glasses to acetic acid increases substantially when Li_2O is introduced.

On the whole the glasses studied are distinguished by high acid resistance and they meet the requirements for the CLTE and flowability for glass enamel coatings. At 820°C the experimental glasses all formed coatings with no visible defects and with good sheen and continuity but with different degrees of whiteness (see Table 1).

It is known [4] that the degree of whiteness of titanium-containing coatings is determined mainly by the precipitated crystalline phase — anatase imparts greater brightness than rutile to coatings.

X-ray phase analysis of the experimental glasses established the regions of precipitation of the crystalline phase

TABLE 1.

Glass (see Fig. 1)	Flowability, mm	CLTE, 10^{-7} K^{-1}	Softening onset temperature, °C	Whiteness, %	Mass losses in 4% acetic acid
1	30.9	84.00	575	60	0.11
2	35.0	85.70	565	62	0.09
3	38.0	88.23	557	64	0.13
4	41.0	91.55	561	63	0.13
5	44.0	93.40	560	62	0.125
6	33.9	86.00	567	68	0.10
7	41.0	85.89	552	78	0.04
8	51.6	87.30	546	78	0.09
9	56.0	90.80	550	77	0.10
10	54.0	92.90	544	76	0.15
11	51.7	87.00	544	80	0.12
12	56.9	86.36	542	84	0.075
13	54.7	88.17	544	83	0.05
14	54.0	90.00	544	82	0.06
15	37.3	88.00	534	76	0.14
16	37.9	89.10	534	74	0.05
17	43.0	89.00	537	73	0.085

formed as a result of the heat treatment of the glass powders at 820°C for 10 min. The temperature 820°C was chosen as the average value of the optimal temperature for fast annealing of titanium coatings. The main phases that precipitate during heat treatment are anatase, rutile, and small quantities of various modifications of quartz.

When potassium oxide is substituted for sodium oxide the whiteness of a coating remains essentially unchanged at the level 60 – 64%, and in heat-treated glasses rutile precipitates in this section (see Fig. 1). The introduction of 2 – 4% Li_2O increases the whiteness of the coatings to 80 – 84%, and the increase is greatest when Na_2O and K_2O are present in the glass. Anatase crystallizes predominately when such glasses are heat-treated. Increasing the Li_2O content to 6% decreases the whiteness of the coating to 73 – 76%, and rutile and small quantities of quartz-like phases are observed to be present in heat-treated glasses.

Our investigations show that changing the ratio of the alkali metal oxides in titanium-containing glass permits regulating the properties of the glass over wide limits. The optimal glass compositions are (%): 2 – 4 K_2O, 2 – 4 Li_2O, 8 – 12 Na_2O. Lithium oxide present in amounts 2 – 4% has the best effect on the flowability and acid-resistance of glass, the annealing temperature, and coating whiteness. Introducing three alkali oxides into glass decreases the viscosity of the melts and correspondingly the temperature of coating formation, which permits decreasing the content of boron oxide in titanium-containing enamels.

As a result of these investigations, a composition has been developed for white glass enamel, laboratory tests have been performed, and the main technological and operational characteristics have been determined.

CLTE, $10^{-7}\ K^{-1}$	86.5
Softening onset temperature, °C	530
Flowability, mm	47
Coating whiteness, %	84
Corrosion resistance in 4% acetic acid, $mg/(cm^2 \cdot h)$	0.037
Boron ion migration from a coating into a 4% acetic acid solution, mg/liter	0.28

In summary, the effect of the ratio of alkali metals on the properties of glass enamels has been determined and the optimal alkali-metal concentrations have been determined. The partial substitution of lithium oxide for sodium oxide increases the acid-resistance of the glasses, promotes the crystallization of anatase during annealing of the coatings, and increases the whiteness of the coatings. The enamel which is optimal with respect to the technological and physical – chemical properties (flowability, CLTE, and whiteness) meets the requirements for covering enamels for steel utensils. The corrosion resistance and the very low migration of boron into acetic-acid extracts of the glass enamel which has been developed are better than those of existing commercial analogues.

REFERENCES

1. A. A. Appen, *The Chemistry of Glass* [in Russian], Khimiya, Leningrad (1974).
2. S. P. Rodtsevich, S. Yu. Eliseev, and V. V. Tavgen', "Low-melting, chemically stable enamel for steel utensils," *Steklo Keram.*, No. 1, 25 – 27 (2003).
3. V. V. Tavgen', S. P. Rodtsevich, and T. S. Minkevich, "Alkali titanium-containing glass for white glass enamels with high corrosion resistance," *Steklo Keram.*, No. 7, 31 – 33 (2005).
4. V. V. Vargin, *Enameling of Metal Articles* [in Russian], Mashinostroenie, Leningrad (1972).